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COMPRESSION-SET BEHAVIOR
OF
IRRADIATED SILICONE ELASTOMERS

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COMPRESSION-SET BEHAVIOR
OF
IRRADIATED SILICONE ELASTOMERS

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GENERAL DYNAMICS | FORT WORTH

ABSTRACT

The effect of nuclear radiation (five different dose levels in the range of from 10^8 to 10^{10} ergs/gm(C)) on the compression-set behavior of three types of silicone elastomers (SE-551, SE-361, and DC-675) was examined. During the irradiation, the samples were compressed at constant strain in an air environment. The observed postirradiation percent compression set after an accumulated dose is described by an empirically derived equation.

The ratio of the number of network chains at equilibrium with the unstrained thickness to the number of network chains at equilibrium with the applied strain rapidly decreases with dose.

The Shore-A hardness of these elastomers was observed to increase with dose. Within the dose region investigated, the hardness attained after an accumulated dose can be expressed by an empirically derived equation.

REPORT SUMMARY

Compression set buttons of three types of silicone elas-
tomers (SE-361, SE-551, and DC-675) were irradiated to five
different dose levels in the range of from 10^8 to 10^{10} ergs/
gm(C) in the GD/FW Ground Test Reactor. During irradiation
the samples were compressed at constant deflection in an air
environment. Experimental data are given for percent compres-
sion set and Shore A hardness changes as a function of radia-
tion dose. It was found that the compression set could be
described by the equation

$$S_D = S_m \exp\left\{-\alpha D^{-n}\right\}$$

where S_D = percent compression set at dose D $\left[\text{ergs/gm(C)}\right]$,

S_m = percent compression set $D \longrightarrow$, and

α, n = material parameters (the values calculated
for α: 0.322, 0.478, and 0.250; and for n:
0.671, 0.822, and 0.905 for SE-361, SE-551,
and DC-675, respectively.)

This equation was also applied with good results to data
from the B. F. Goodrich Research Center for radiation-induced
compression set for different types of elastomers.

According to the concept of Andrews,Tobolsky and Hansen,
two principal species of network chains are postulated for a
polymer network relaxing under compression: (1) chains that
are at equilibrium when the sample is in its undeformed state,
N_o, and (2) chains formed by the agency of radiation that are
at equilibrium in the strained state, N_α. It can be shown

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that the network chain ratio $\zeta = N_O/N_\alpha$ is given by

$$\zeta = \frac{(t_\alpha/t_s) - (t_s/t_\alpha)^2}{(t_s/t_O)^2 - (t_O/t_s)}$$

where t_O = original thickness of sample,

t_α = thickness to which sample is compressed, and

t_s = thickness of sample after release from com-
pression.

The quantity ζ rapidly decays with dose, and at very high doses it tends asymptotically toward a small negative value, indicating that chain species other than those postulated become operative.

Finally, the observed Shore A hardness can be expressed by the relation

$$H_D = H_O (D/D_O)^c \text{ for } D \geqslant D_O$$

where H_D = hardness attained after dose $D \left[\text{ergs/gm(C)} \right]$,

H_O = hardness of the unirradiated sample,

D_O = virtual dose, i.e., the extrapolated inflection
point at which the sample's hardness begins to
change, and

c = material parameter.

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I. INTRODUCTION

Compression set can be defined as the deformation perma-
nently remaining in a specimen after it has been subjected to
a compressive stress for a specified period of time. Since
the compression-set process is sensitive to chain scission and
crosslinking reactions, and since high-energy radiation can
produce both these reactions, the study of compression set in
elastomers provides a good method of determining their radia-
tion resistance.

In the present investigation, the compression-set be-
havior of three silicone elastomers was studied as a function
of radiation dose. Previous experimental data on this behavior
were mostly obtained over too narrow a dose range. This made
it difficult to develop predictive relationships for the entire
course of radiation-induced compression set.

The principal objective of this study was to gain data on
compression-set behavior of silicone elastomers over an extended
range of dose and, if possible, to derive quantitative relation-
ships describing this behavior. Empirical expressions of this
sort have been reported in the literature (Refs. 1 and 2). They
are particularly useful for comparative and predictive purposes.

An additional endeavor of this investigation was to deduce
from the experimental results certain information about the un-
derlying molecular processes by employing the concepts of the
theory of rubberlike elasticity.

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II. EXPERIMENTAL METHOD

2.1 Sample Preparation

Three different types of polysiloxane elastomers, (General Electric SE-551, General Electric SE-361, and Dow Corning Silastic 675) were investigated in the form of standard ASTM compression-set buttons of cylindrical shape, 0.5 inch thick and about 1.129 inches in diameter.

SE-551 is a methyl-phenyl polysiloxane compounded with both a manufactured silica and a diatomaceous earth type of silica and colored with Titanox. Approximately 40% of SE-551 consists of filler materials.

SE-361 is a methyl-vinyl polysiloxane, also compounded with both a manufactured silica and a diatomaceous earth type of silica and colored with red iron oxide. About 45% of the total composition consists of filler.

Dow Corning Silastic DC 675 is a methyl-phenyl polysiloxane of 7.5 mole % penyl methyl siloxane units and 92.5 mole % dimethyl siloxane units. Its average molecular weight is about 4×10^5 - 6×10^5.

Complete recipes and curing histories of the aforementioned polysiloxane vulcanizates could not be ascertained because of proprietary reservations.

Of each type of elastomer, a set of 35 compression-set samples was prepared in conformance with ASTM procedure D-395-55. In each such set, 10 samples were selected as control specimens, while 5 samples were used for each of the five irradiation conditions.

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The thickness, the specific gravity, and the Shore A hardness of the samples were measured prior to compression and irradiation. The thickness was determined by averaging five individual measurements on each sample (i.e., one measurement at each of the four quadrants of the sample's periphery and one in its center). The Shore A hardness values constitute the average of three individual measurements on each sample. The specific gravity of the elastomers used was determined on the basis of weight-in-air and weight-in-water measurements.

All samples were then compressed in devices as prescribed by procedure ASTM D395-55, Method B (Ref. 3). In the present investigation, the standard ASTM procedure was modified in the following respects: (1) Compression plates of 60-61T aluminum alloy were used instead of chrome-platedsteel plates to minimize handling problems due to activation of the metal jigs in a neutron field. (2) The spacer thickness was not selected according to the hardness of the rubber, as outlined in step b of Reference 3, because spacers of the required thicknesses were not available; instead, spacers of 0.376+, 0.377-, and 0.378-inch thickness were used randomly for all three types of elastomers and the percentage deflection was calculated for each specimen. (3) The heat treatment (step c of Reference 3) in the procedure was omitted, and the radiation treatment was substituted.

The SE-551 samples were compressed 18 hours before irradiation and the SE-361 and the DC-675 samples were compressed 12 hours before irradiation. All samples were released approximately 216 hours after irradiation. The total time that the

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specimens were in compression was approximately 240 hours for the SE-551 samples and 234 hours for the SE-361 and DC-675 samples. The control samples were compressed for the same periods of time and stored in the laboratory at 75°F.

The samples to be irradiated were mounted on five perforated aluminum panels in a circular configuration at an average distance of eight inches from the center point, which corresponded to the reactor centerline when the panels were inserted. Five compression-set buttoms of each elastomer were mounted on each panel.

2.2 Dosimetry

Four dosimetry packets were mounted in the circular configurations on each panel, eight inches from the center and at equidistant locations in each of the four quadrants of the circle. The dosimeters contained in each of the four packets on the five panels are given in Table I. The location of Panels 1 and 2 was inadvertently interchanged. The original plan was that Panel 2 should receive the lowest dose, while Panel 1 was to be exposed to the next highest dose. For this reason, Panel 1 was equipped with two types of gamma-ray dosimeters to record a dose that was expected to be close to the upper limit of usefulness of the tetrachloroethylene system and to the lower limit of the nitrous-oxide system.

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Table I

Dosimetry Description

Dosimeter		Contents of Dosimetry Packets on Panel				
Type	Radiation Detected	1	2	3	4	5
Aluminum foil	Neutrons (E > 8 Mev)	X	X	X	X	X
Sulfur pellet	Neutrons (E > 2.9 Mev)	X	X	X		
Sulfur-epoxy disk	Neutrons (E > 2.9 Mev)				X	X
Pair of bare and cadmium-covered copper foils	Thermal neutrons	X	X	X	X	X
Nitrous-oxide ampoule	Gamma rays	X		X	X	X
Tetrachloro-ethylene ampoule	Gamma rays	X	X			

2.3 Sample Irradiation

The sample irradiation was carried out in the Radiation
Effects Testing System at GD/FW's Nuclear Aerospace Research
Facility (NARF). In this system, the Ground Test Reactor (GTR)
is used as the radiation source. It is located in one side
(the west side) of a pool divided by a dam wall into a wet and
dry side. The dry side of the pool is the irradiation cell.
The GTR is positioned in a closet-like structure that is built
into the center of the dam and protrudes into the irradiation
cell. Thus, three faces of the closet (the GTR) are available
for irradiation testing.

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The materials, components, or systems that are to be tested are placed in environmental chambers that are transported on pallets down into the irradiation cell by a remotely controlled three-track shuttle system. Temperatures inside the chambers are controlled (-65°F to 450°F) from an air duct system that terminates beneath the pallets at the three testing positions.

Two environmental chambers were used during the tests described here. Panels 1 and 2 were irradiated in one chamber for 2.5 hours at 0.6 Mw reactor power, while Panels 3, 4, and 5 were exposed in a second chamber for 5 hours at 3 Mw. The locations were selected in such a manner that the five panels would receive gamma-ray doses in the range of from 10^8 to 10^{10} ergs/gm(C). The irradiation was carried out in an air environment, and the temperature was monitored by a thermocouple embedded within a compression-set button of silicone rubber mounted on each panel. An attempt was made to maintain the temperature within these monitored samples as close to 75°F as possible by circulating a refrigerated-air current in the environmental chambers. This was achieved for the samples mounted on Panels 1, 2, and 3. However, the temperature as monitored in the samples on Panels 4 and 5, which received the two higher dose rates (see Table III), could not be held constant despite the fact that the ambient air had been cooled to 40°F. Radiation-induced heating produced an appreciable temperature rise in the monitored samples of these two panels. Within a period of about 75 minutes after the reactor had been brought to peak power, the temperatures recorded for

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Panels 4 and 5 had risen to 120°F and 200°F, respectively, and remained at these levels with short fluctuations of $\pm$ 10°F until reactor shutdown.

2.4 Sample Testing

About 216 hours after termination of the irradiation, all samples were released from the compression devices. The thickness of the samples was determined 30 minutes after release. The thickness values of each sample constitute the average of five individual measurements as described in Section 2.1. The Shore A hardness values are the average of three individual measurements per sample.

The percent deflection was calculated as follows:

$$\%D \ = \ \frac{t_o - t_\alpha}{t_o} \ X \ 100$$

where t_o = original thickness and t_α = thickness of the spacer.

The percent compression set was calculated as follows:

$$\%S \ = \ \frac{(t_o - t_s)}{(t_o - t_\alpha)} \ X \ 100$$

where t_o = original thickness of the sample,

t_s = thickness of the sample 30 minutes after release from the compression device, and

t_α = thickness to which the sample was compressed (spacer thickness).

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III. EXPERIMENTAL RESULTS

Panels 1 and 2 were irradiated for 2.5 hours at 0.6 Mw reactor power and Panels 3, 4, and 5 were irradiated for 5 hours at 3 Mw reactor power. The dosimeters mounted on the panels yielded the dose values listed in Table II. The average rates of irradiation are given in Table III.

The preirradiation values of the specific gravity of the three elastomers were as follows:

Elastomer	Specific Gravity
SE-361	1.27
SE-551	1.23
DC-675	1.26

The hardness of each sample was measured both before and after irradiation and the resultant data are presented in Table IV.

The thickness of the compression-set buttons measured before compression and 30 minutes after release from the compression device, the percent deflection during compression, and the percent compression set calculated from these measurements are given in Tables V, VI, and VII, for elastomers SE-361, SE-551, and DC-675, respectively. The average values and the standard deviation of the measurements are also given.

Table II

Dosimetric Data of Silicone Elastomer Irradiation

Integrated Neutron Flux (n/cm^2 x 10^{12})			Absorbed Gamma-Ray Dose [ergs/gm(C) x 10^{-9}]	
Aluminum Foil (E > 8 Mev)	Sulfur (E > 2.9 Mev)	Copper foils bare-Cd-cov. (thermal neut)	Nitrous oxide	Tetrachloro-ethylene
Panel 1				
1.38	33.3	11.4	0.168	0.219
1.38	31.8	9.07	0.244	0.219
1.35	32.6	11.9	0.261	0.210
1.34	32.1	11.1	0.244	0.219
Average 1.36 ± 0.02	Average 32.5 ± 0.66	Average 10.9 ± 1.22	Combined Average 0.222 ± 0.030	
Panel 2				
3.03	71.8	9.88	-----	0.455
3.20	76.9	18.3	-----	0.465
3.59	88.1	11.2	-----	0.517
3.21	73.4	8.75	-----	0.455
Average 3.26 ± 0.231	Average 77.6 ± 7.35	Average 12.0 ± 4.30		Average 0.473 ± 0.033
Panel 3				
9.40	251	90.2	1.51	-----
9.29	262	97.7	1.89	-----
9.40	257	----	1.58	-----
10.8	252	----	1.60	-----
Average 9.72 ± 0.72	Average 256 ± 5.5	Average 94.0 ± 5.3	Average 1.65 ± 0.17	
Panel 4				
41.0	1230	81.2	5.08	-----
41.5	1230	61.6	4.91	-----
42.6	1380	62.6	5.08	-----
38.6	1410	109	4.91	-----
Average 40.9 ± 1.7	Average 1310 ± 95	Average 78.8 ± 22.2	Average 5.00 ± 0.095	
Panel 5				
106	3320	-----	13.8	-----
105	3470	-----	14.0	-----
106	3270	-----	12.0	-----
-----	3120	-----	-----	-----
Average 106	Average 3300 ± 145		Average 13.2 ± 1.14	

Table III

Rate of Irradiation of Silicone Elastomers

Panel	Neutron Flux n/cm^2-sec x 10^{-9}	Gamma-Ray Dose Rate ergs/gm(C)-hr x 10^{-9}
1	0.151 (E > 8 Mev) 3.61 (E > 2.9 Mev) 1.21 thermal	0.088
2	0.362 (E > 8 Mev) 8.61 (E > 2.9 Mev) 1.33 thermal	0.189
3	0.540 (E > 8 Mev) 14.2 (E > 2.9 Mev) 5.22 thermal	0.33
4	2.27 (E > 8 Mev) 73.0 (E > 2.9 Mev) 4.37 thermal	1.00
5	5.87 (E > 8 Mev) 183. (E > 2.9 Mev)	2.64

Table IV

Pre- and Postirradiation Shore A Durometer Hardness
of Silicone Elastomers

Elastomer	Gamma-Ray Dose $[\text{ergs/gm(C)} \times 10^{-9}]$									
	0	0.222	0	0.473	0	1.65	0	5.0	0	13.3
SE-361	42	54	47	62	48	72	48	86	50	95
	50	58	47	62	49	73	49	86	50	94
	50	57	49	63	44	70	50	86	50	94
	51	57	49	63	49	72	48	86	50	94
	50	57	48	62	48	74	47	86	50	93
	48.6	56.6	48.0	62.4	47.6	72.2	48.4	86.0	50	94
	±3.7	±1.5	±1.0	±0.5	±2.1	±1.5	±1.1	0	0	±0.7
SE-551	43	43	41	46	41	57	43	72	43	88
	42	42	42	48	42	57	44	72	43	87
	43	44	42	46	42	57	43	73	43	87
	42	42	42	46	44	56	43	72	44	85
	44	43	43	47	44	56	41	71	44	87
	42.8	42.8	42.0	46.6	42.6	56.6	42.8	72.0	43.4	86.8
	±0.8	±0.8	±0.7	±0.9	±1.3	±0.5	±1.1	±0.7	±0.5	±1.1
DC-675	68	68	66	73	68	85	68	94	68	98
	67	64	67	72	69	84	68	94	67	98
	66	67	68	70	68	83	69	95	57	98
	66	65	68	72	68	84	67	94	65	99
	68	67	66	70	67	83	68	94	68	97
	67.0	66.2	67.0	71.4	68.0	83.8	68.0	94.2	67.0	98.0
	±1.3	±1.6	±1.3	±1.3	±0.7	±2.6	±0.7	±0.6	±1.2	±0.7

Table V

Compression Set of Silicone Elastomer SE-361

Gamma Ray Dose $[\text{ergs/gm}(C) \times 10^{-9}]$	Sample Thickness (inch)		Spacer Thickness (inch)	Deflection (%)	Compression Set (%)
	Before	After			
Control	0.496	0.486	0.377	24.0	8.40
	0.488	0.487	0.377	22.7	0.90
	0.488	0.482	0.377	22.7	5.41
	0.493	0.486	0.377	23.5	6.03
	0.489	0.484	0.377	22.9	4.46
	0.484	0.480	0.377	22.1	3.74
	0.487	0.482	0.377	22.6	4.55
	0.496	0.492	0.377	24.0	3.36
	0.481	0.476	0.377	21.6	4.81
	0.491	0.485	0.377	23.2	5.26
					4.69±2.76
0.222	0.487	0.437	0.376	22.8	45.05
	0.484	0.437	0.376	22.3	43.52
	0.498	0.443	0.376	24.5	45.08
	0.486	0.438	0.376	22.6	43.64
	0.483	0.437	0.376	22.2	42.99
					44.06±0.95
0.473	0.486	0.419	0.378	22.2	62.04
	0.494	0.419	0.378	23.5	64.66
	0.485	0.413	0.378	22.1	67.29
	0.488	0.417	0.378	22.5	64.55
	0.494	0.421	0.378	23.5	62.93
					64.29±2.01
1.65	0.497	0.396	0.378	24.0	84.87
	0.487	0.394	0.378	22.4	85.32
	0.485	0.392	0.378	22.1	86.92
	0.483	0.394	0.378	21.7	84.76
	0.488	0.391	0.378	22.5	88.18
					86.01±1.49
5.0	0.491	0.378	0.376	23.4	98.26
	0.486	0.387	0.376	22.6	90.00
	0.484	0.376	0.376	22.3	100.00
	0.489	0.380	0.376	23.1	96.46
	0.490	0.376	0.376	23.3	100.00
					96.94±4.15
13.3	0.486	0.373	0.378	22.2	104.63
	0.480	0.368	0.378	21.3	109.80
	0.487	0.370	0.378	22.4	107.34
	0.496	0.367	0.378	23.8	109.32
	0.499	0.366	0.378	24.2	109.92
					108.20±2.12

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Table VI

Compression Set of Silicone Elastomer SE-551

Gamma Ray Dose [ergs/gm(C) x 10^{-9}]	Sample Thickness (inch)		Spacer Thickness (inch)	Deflection (%)	Compression Set (%)
	Before	After			
Control	0.480	0.476	0.378	21.2	3.92
	0.481	0.478	0.378	21.4	2.91
	0.484	0.480	0.378	21.9	3.77
	0.493	0.487	9.378	23.3	5.22
	0.479	0.477	0.378	21.1	1.98
	0.489	0.486	0.378	22.7	2.70
	0.484	0.481	0.378	21.9	2.83
	0.490	0.485	0.378	22.9	4.46
	0.495	0.489	0.378	23.6	5.13
	0.491	0.486	0.378	23.0	4.42
					3.73±1.22
0.222	0.491	0.467	0.378	23.0	21.24
	0.489	0.461	0.378	22.7	25.22
	0.495	0.465	0.378	23.6	25.64
	0.487	0.462	0.378	22.4	22.94
	0.483	0.458	0.378	22.6	23.80
					23.77±1.78
0.473	0.492	0.442	0.378	23.2	43.86
	0.496	0.445	0.378	23.8	43.22
	0.488	0.442	0.378	22.5	41.82
	0.495	0.441	0.378	23.6	46.15
	0.494	0.445	0.378	23.5	42.24
					43.46±1.71
1.65	0.495	0.408	0.378	23.6	74.36
	0.488	0.409	0.378	22.5	71.82
	0.500	0.408	0.378	24.4	75.41
	0.488	0.408	0.378	22.5	72.73
	0.478	0.410	0.378	20.9	68.00
					72.46±2.86
5.0	0.484	0.382	0.378	21.9	96.23
	0.490	0.385	0.378	22.9	93.75
	0.494	0.383	0.378	23.5	95.69
	0.502	0.382	0.378	24.7	96.77
	0.497	0.382	0.378	23.9	96.64
					95.82±1.23
13.3	0.491	0.369	0.378	23.0	107.96
	0.482	0.372	0.378	21.6	105.77
	0.492	0.369	0.378	23.2	107.89
	0.486	0.367	0.378	22.2	110.19
	0.487	0.374	0.378	22.4	103.67
					107.10±2.47

Table VII

Compression Set of Silicone Elastomer DC-675

Gamma-Ray Dose [ergs/gm(C) x 10^{-9}]	Sample Thickness (inch)		Spacer Thickness (inch)	Deflection (%)	Compression Set (%)
	Before	After			
Control	0.498	0.495	0.377	24.3	2.48
	0.497	0.495	0.377	24.1	1.66
	0.504	0.500	0.377	25.2	3.15
	0.508	0.506	0.377	25.8	1.53
	0.500	0.500	0.377	24.6	0.00
	0.491	0.489	0.377	23.2	1.75
	0.495	0.492	0.377	23.8	2.54
	0.494	0.491	0.377	23.7	2.56
	0.495	0.495	0.377	23.8	0.00
	0.484	0.481	0.377	22.1	2.80
					1.85±0.30
0.222	0.497	0.453	0.378	23.9	36.97
	0.488	0.451	0.378	22.5	33.64
	0.498	0.451	0.378	24.1	39.17
	0.491	0.451	0.378	23.0	35.40
	0.487	0.442	0.378	22.8	40.54
					37.14±2.79
0.473	0.488	0.412	0.378	22.5	69.09
	0.506	0.422	0.378	25.3	65.63
	0.497	0.427	0.378	23.9	58.82
	0.495	0.422	0.378	23.6	62.39
	0.501	0.428	0.378	24.6	59.35
					63.06±4.33
1.65	0.495	0.392	0.378	23.6	88.03
	0.497	0.394	0.378	23.9	86.55
	0.495	0.392	0.378	23.6	88.03
	0.493	0.391	0.378	23.3	88.70
	0.480	0.393	0.378	21.3	85.29
					87.32±1.38
5.0	0.499	0.380	0.376	24.6	96.75
	0.488	0.378	0.376	23.0	98.21
	0.499	0.384	0.376	24.6	93.50
	0.504	0.382	0.376	25.4	95.31
	0.497	0.381	0.376	24.3	95.87
					95.93±1.74
13.3	0.492	0.371	0.378	23.2	106.14
	0.499	0.375	0.378	24.2	102.48
	0.496	0.376	0.378	23.8	101.69
	0.506	0.374	0.378	25.3	103.13
	0.474	0.382	0.378	20.3	95.83
					101.85±3.77

IV. DISCUSSION OF RESULTS

4.1 Compression-Set Analysis

4.1.1 Empirical Relationships

Analysis of the experimental data of this investigation showed that the radiation-induced compression-set behavior of the three polysiloxane elastomers could be described by the equation

$$S_D = S_m \exp\left[-\alpha D^{-n}\right] \tag{1}$$

where

S_D = percent compression set at dose D $\left[ergs/gm(C)\right]$,

S_m = percent compression set at $D \longrightarrow \infty$, and

α, n = material parameters.

On the basis of a least-squares fit of the experimental data, the numerical values of the material parameters were determined as follows:

for SE-361, $\alpha = 0.322$, $n = 0.671$

for SE-551, $\alpha = 0.478$, $n = 0.822$

for DC-675, $\alpha = 0.250$, $n = 0.905$

Figure 1 shows a plot of Equation 1 for each elastomer investigated together with the experimental data points.

In order to determine whether this empirically derived equation could be satisfactorily applied to other compression-set data, B. F. Goodrich Research Center data (Ref. 1) for ten different elastomers irradiated in the MTR Gamma Facility were

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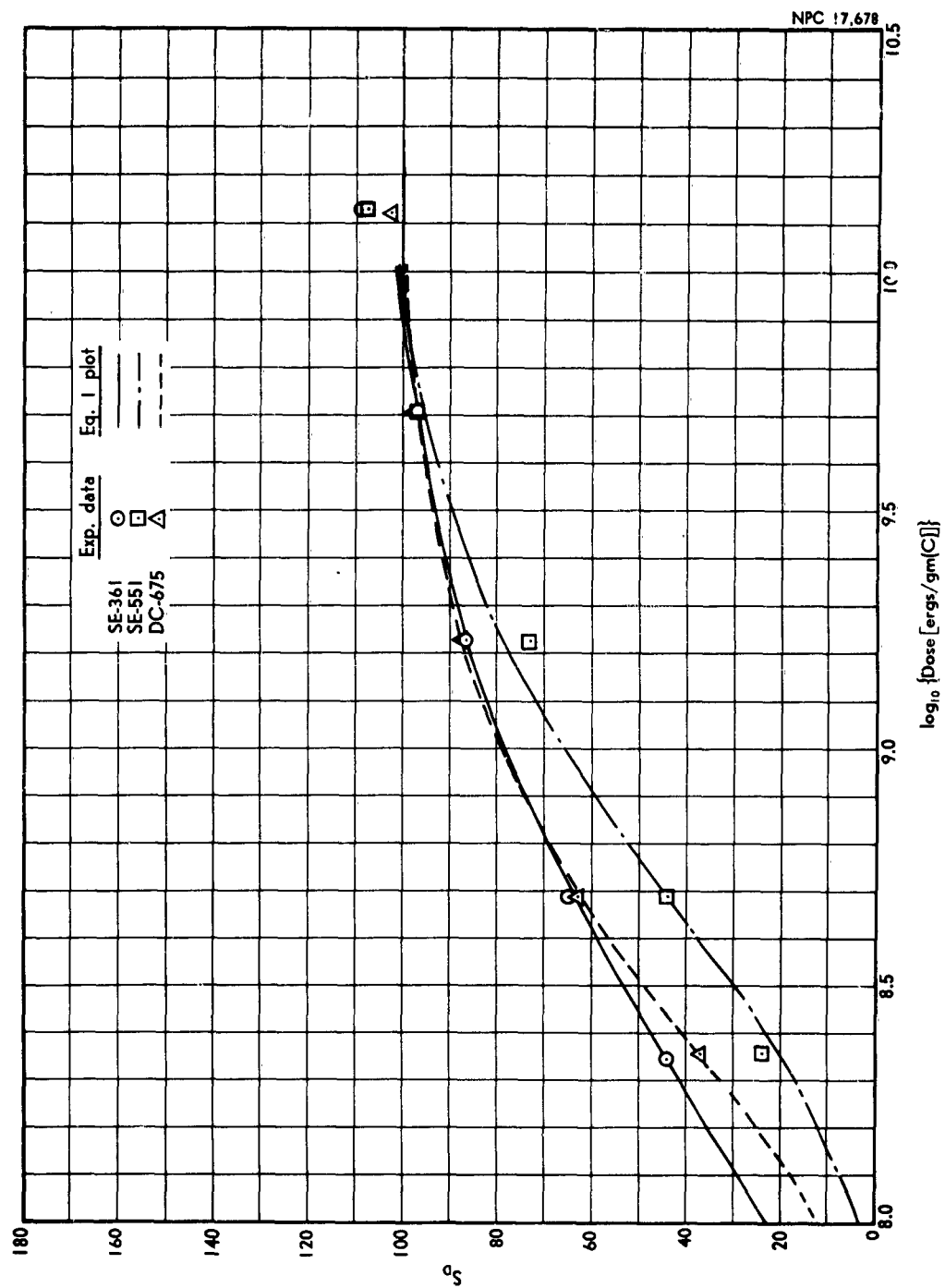
Figure 1. Compression Set of Three Silicone Elastomers as a Function of Absorbed Gamma-Ray Dose

used. The material parameters of n and α were determined by
the least-squares method. The results of this analysis are
presented in Table VIII together with the experimental data.
The base recipes of the ten selected elastomers are given
in Table IX. In most instances, Equation 1 provides a rea-
sonably good description of the observed compression-set
behavior.

4.1.2 Molecular Interpretation

The phenomenon of compression set can be caused by a
variety of molecular relaxation processes. When a three-
dimensional polymer is placed under constant deformation,
the initial decay of stress is due principally to relaxa-
tion of secondary bonds. This process is reversible, i.e.,
upon removal of the deforming stress, the sample returns to
its original shape. In addition, physical or chemical agencies
may cause primary bonds within the chain molecules to rupture,
thus allowing the whole system to relax irreversibly under
external stress. In the case of constant deformation, the
macroscopic effect of such chain scission is evidenced in a
slow irreversible decay of stress, which ultimately approaches
zero in an asymptotic fashion. If crosslinking occurs simul-
taneously while the sample is held at constant strain, the
equilibrium shape gradually shifts from the original shape
of the unstrained sample to the shape of the strained sample.
Since high-energy radiation induces both chain scission and
crosslinking reactions in high polymers, compression-set be-
havior in a radiation field is a sensitive function of dose.

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Table VIII

Radiation-Induced Compression-Set Behavior of Ten Selected Elastomers

B. F. Goodrich Compound*	Gamma-Ray Dose $[ergs/gm(C) \times 10^{-9}]$	% Compression Set		Parameter	
		Measured	Calculated	n	α

Hycar 1001
Base recipe 1
  Curative:
  Altax - 3.0 pts. by wt.
  Sulfur - 2.0 pts. by wt.
  Cure: 15 min at 293°F
	.089
	.871
	2.18
	4.37
	10.5
		30.7
		58.2
		70.6
		81.5
		88.1
			26
			63
			74
			80
			87
				0.466	0.432

Hycar 1001
  Same as above except
  Cure: 45 min at 293°F
	.089
	.871
	2.18
	4.37
	10.5
		12.9
		41.6
		57.5
		69.7
		83.6
			10
			46
			61
			71
			80
				0.495	0.707

Hycar 1001
Base recipe 1
  Curative:
  Hydrated lime - 4.0 pts.
        by wt.
  DCP - 1.5 pts. by wt.
	.089
	.871
	2.18
	4.37
	10.5
		8.5
		36.9
		56.1
		70.9
		85.9
			2
			44
			61
			71
			82
				0.565	0.749

Hycar 1001
Base recipe 1
  Curative:
  Amberol ST 12 pts. by wt.
  Stannous chloride - 1.5 pts
        by wt.
	.089
	.871
	2.18
	4.37
	
	10.5
		9.9
		44.5
		66.1
		81.0
		
		91.4
			6
			53
			71
			81
			
			89
				0.668	0.565

Hycar 1001
Base recipe 1
  Curative:
  Polyac - 2.0 pts. by wt.
	.089
	.871
	2.18
	4.37
	10.5
		35.4
		68.5
		82.5
		90.0
		93.4
			31
			73
			83
			89
			93
				0.585	0.282

Natural Rubber Base recipe 2	.087 .438 .868 4.36 10.5	13.7 22.9 36.2 75.3 88.5	5 33 54 75 85	0.601	0.668
Neoprene GN Base recipe 3	.088 .871 2.18 4.36 10.4	4.6 38.9 59.9 76.5 90.4	3 46 67 77 87	0.692	0.696

Hycar 1001
Base recipe 4
  Antirad:
  Hydroquinone/Antiox 4010
  (50/50) - 5 phr
	.087
	.438
	.868
	4.36
	10.5
		8.6
		13.4
		21.9
		51.3
		73.2
			3
			19
			34
			54
			66
				0.432	1.13

SBR 1500/1501
Base recipe 5
  Antirad:
  Antiox 4010 - 5 phr
	.087
	.438
	.868
	4.36
	10.5
		4.0
		13.3
		23.2
		55.3
		76.9
			2
			17
			35
			59
			73
				0.546	1.13

Hypalon 20
Base recipe 6
  Antirad:
  Hydroquinone/Antiox 4010
  (50/50) - 5 phr
	.088
	.871
	2.18
	4.36
	10.4
		18.1
		45.4
		55.7
		70.5
		85.0
			13
			50
			63
			71
			81
				0.467	0.649

* Base recipes given in Table IX.　　**28**

Table IX

Base Recipes for B. F. Goodrich Compounds

1	Hycar 1001	100
	SRF Black	50
	Zinc oxide	5
	Stearic acid	0.5
		155.5
2	Natural rubber	100
	Age-Rite Powder	1.0
	EPC Black	50
	Zinc oxide	5.0
	Stearic acid	3.0
	Altax	1.0
	Sulfur	3.0
		163.0
3	Neoprene GN	100
	EPC Black	35
	Zinc oxide	5
	Stearic acid	1
	Magnesium oxide	4
		145.0
4	Hycar 1001	100
	SRF Black	50
	Zinc oxide	5
	Altax	3
	Sulfur	2
		160.0
5	SBR-1500/1501	100
	EPC Black	40
	Zinc oxide	5
	Stearic acid	1.5
	Altax	3.0
	Sulfur	2.0
		153.5
6	Hypalon 20	100
	HAF Black	20
	Rosin	2.5
	Tetrone A	1.0
	Magnesium oxide	30
		153.5

For the largest radiation dose employed in this study 1.33 x 10^10 ergs/gm(C) , the samples actually showed a volume contraction when released from the compressive devices. This contraction is most likely attributable to the extremely high crosslinking density attained at that dose.

The behavior of a three-dimensional polymer network relaxing under compression may be viewed, according to the concept of Andrews, Tobolsky, and Hansen (Ref. 4), as a competition principally between two types of chains: (1) chains that are at equilibrium when the sample is in its original undeformed state (i.e., at $t - t_o$), and (2) chains formed by the agency of radiation that are at equilibrium in the strained state (i.e., at $t = t_\alpha$). If N_O is the number of network species of Type 1 per cm^3 of elastomer and N_α is the number of network species of Type 2 per cm^3 of elastomer, then, applying the kinetic theory of rubberlike elasticity of this model, the stresses developed by these two species of network chains are respectively

$$\sigma_o = N_o \, k \, T\left[\left(\frac{t_s}{t_o}\right)^2 - \frac{t_o}{t_s}\right] \tag{2}$$

$$\sigma_\alpha = N_\alpha \, k \, T\left[\left(\frac{t_s}{t_\alpha}\right)^2 - \frac{t_\alpha}{t_s}\right] \tag{3}$$

where σ_o = stress exerted by the network chains, N_o, tending to restore the sample to its original thickness t_o,

σ_α = stress exerted by the network chains, N_α, tending to retract the sample to the equilibrium position for the chains N_α at t_α,

T = temperature ($^{\circ}$K), and

k = Boltzmann's constant.

As a consequence of the balance between the two oppositely directed stresses associated with these two network species, the sample assumes a shape intermediate between their two equilibrium positions. That is

$$\sigma_o = -\sigma_\alpha$$

The network chain ratio $\zeta = N_o/N_\alpha$ is given by

$$\zeta = \frac{(t_\alpha/t_s) - (t_s/t_\alpha)^2}{(t_s/t_o)^2 - (t_o/t_s)} \tag{4}$$

where t_o = original thickness of the sample,

t_α = thickness to which the sample is compressed, and

t_s = thickness of the sample after release from compression.

Calculations of the N_o/N_α ratio for the three silicone elastomers studied at the various doses is presented in Table X. The change in the ratio as a function of absorbed dose in shown in Figure 2. The quantity ζ rapidly decays with dose, and at very high doses tends asymptotically toward a small negative value, which indicates that chain species other than those postulated in the simple model become operative.

4.2 Hardness Analysis

Finally, the Shore A hardness of these elastomers was observed to increase with dose. Within the dose region investigated, the hardness H_D attained after dose D $\left[\text{ergs/gm}(C)\right]$

28
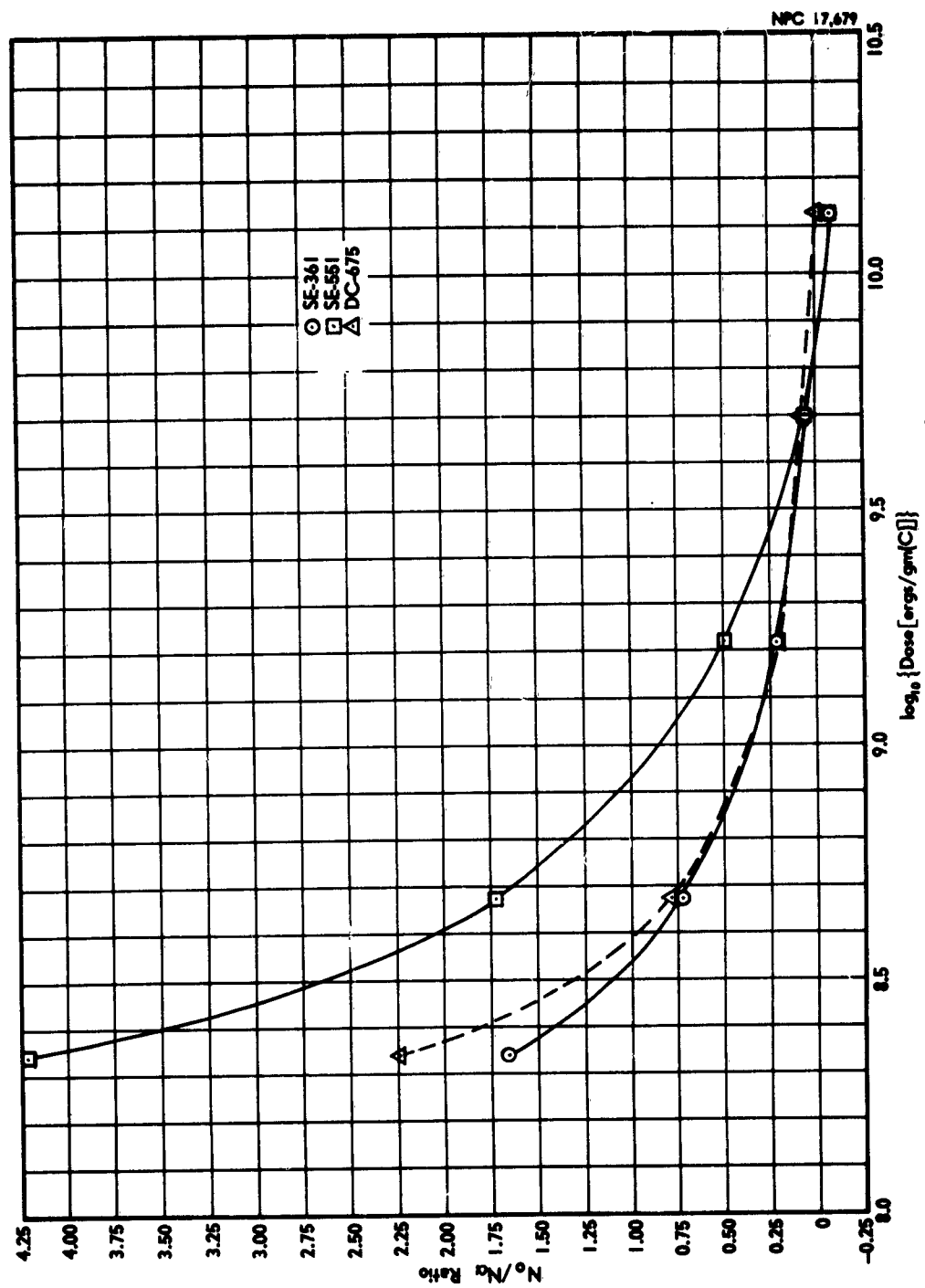
Figure 2. The N_o/N_α Ratio of Three Silicone Elastomers
as a Function of Gamma-Ray Dose

NPC 17,679

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Table X

N_O/N_α Ratio for Three Silicone Elastomers*

Elastomer	Gamma-Ray Dose $\left[\text{ergs/gm(C)} \times 10^{-9}\right]$					
	Control	0.222	0.473	1.65	5.0	13.3
SE-361	38.614	1.653	0.719	0.211	0.042	-0.078
	±38.99	±0.051	±0.202	±0.030	±0.059	±0.069
SE-551	35.921	4.230	1.711	0.489	0.055	-0.082
	±11.92	±0.430	±0.111	±0.064	±0.036	±0.027
DC-675	63.318	2.236	0.776	0.187	0.054	-0.023
	±15.58	±0.309	±0.144	±0.021	±0.077	±0.015

* N_O/N_α = Average value, polymer network chain ratio

could be expressed by the relation

$$H_D = H_0 (D/D_0)^c \text{ for } D \geqslant D_0 \tag{5}$$

where H_0 = Shore A hardness of the unirradiated sample after being compressed,

D_0 = virtual dose, i.e., the extrapolated inflection point at which the sample's hardness begins to change, and

c = material parameter.

Figure 3 presents the experimental values and the curves calculated according to Equation 5. The following values were determined for Equation 5 for the three silicone elastomers:

Elastomer	H_0	$\log_{10} D_0$	c
SE-361	45.7	7.5625	0.1234
SE-551	39.6	8.2625	0.166
DC-675	61.3	7.9026	0.0935
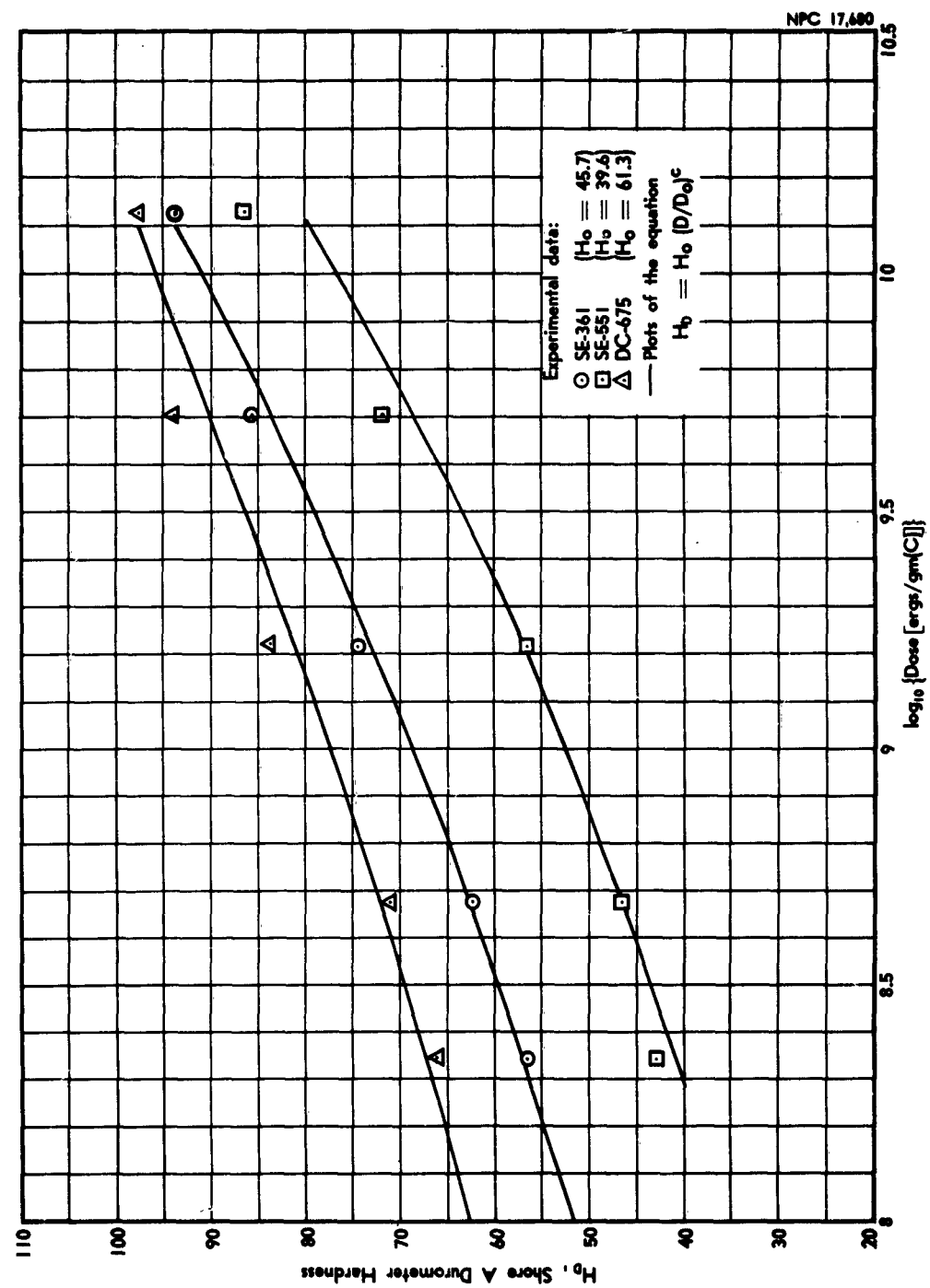
Figure 3. Shore A Durometer Hardness of Three Silicone Elastomers as a Function of Gamma-Ray Dose

4.3 Neutron Contribution

In the foregoing calculations, only the gamma-ray doses recorded were used, and any contribution from the neutrons was neglected. Calculations of the possible neutron contribution to the chemically effective dose in polyethylene were made for this same irradiation and are reported in Reference 5. These calculations indicate that the neutron contribution from this irradiation can be considered negligible for carbon-based polymer chains. Since more energy is required to break Si-Si bonds than C-C bonds, the contribution of the neutrons in producing radiation effects in silicone elastomers should even be less than in polyethylene.

V. CONCLUSIONS

(1) It was shown that three commercial silicone elastomers irradiated in a nuclear reactor field under constant compressive strain in an air environment showed a compression-set behavior that is described by the equation

$$S_D = S_m \exp -\left\{ \alpha \; D^{-n} \right\}$$

where S_D = percent compression set at dose D [ergs/gm(C)],

S_m = percent compression set at $D \rightarrow \infty$, and

α, n = material parameters.

(2) The ratio, ζ , of the number of network chains at equilibrium with the unstrained thickness to the number of network chains at equilibrium with the applied strain rapidly decays with dose and, at very high doses, tends asymptotically towards a small negative value, which indicates that chain species other than those postulated in the simple model become operative.

(3) The Shore-A hardness of these elastomers was observed to increase with dose. Within the dose region investigated, the hardness, H_D, attained after dose [ergs/gm(C)] could be expressed by the relation

$$H_D = H_o \; (D/D_o)^c \; \text{for } D \geqslant D_o$$

where H_o = Shore A hardness of unirradiated sample after compression,

D_o = virtual dose, i.e., the extrapolated inflection point at which the sample's hardness begins to change, and

c = material parameter.

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1. Elastomers, Silanes
2. *Radiation damage
3. *Compressive properties, Creep, Hardness
4. Light-water reactor, Nuclear physics laboratory, Ground Test Reactor, Experimental data

I. Johnson, P. M.
II. Fritz, E. G.
III. Aeronautical Systems Division, Air Force Systems Command
IV. Contract AF33(657)-7201

Nuclear Aerospace Research Facility, General Dynamics/Fort Worth, Fort Worth, Texas. COMPRESSION-SET BEHAVIOR OF IRRADIATED SILICONE ELASTOMERS, by P. M. Johnson and E. G. Fritz. 15 May 1963. 35 p. incl. illus., tables, 5 refs. (NARF-63-2T; MR-N-301)   Unclassified report Contract AF33(657)-7201

The effect of nuclear radiation (five different dose levels in the range of from 10^8 to 10^{10} ergs/gm(C) on the compression-set behavior of three types of silicone elastomers (SE-551, SE-361, and DC-675) was examined. During the irradiation, the samples were compressed at constant strain in an air environment. The observed post-irradiation percent compression set after an accumulated dose is described by an empirically derived equation.

The ratio of the number of network chains at equilibrium with the unstrained thickness to the number of network chains at equilibrium with the applied strain rapidly decreases with dose.

The Shore-A hardness of these elastomers was observed to increase with dose. Within the dose region investigated, the hardness attained after an accumulated dose can be expressed by an empirically derived equation.